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European patent (AT, BE, CH, DE, DK, ES, FR, GB,
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$$(\text{RO})_x \text{P}^{\text{O}} (\text{R}')_y \quad (\text{I})$$

A herbicidal composition which comprises a phosphonate or phosphinate of formula (I), where R and R', which may be the same or different, each represent straight or branch-chained alkyl of 1 to 12 carbon atoms, and x and y are each 1 or 2, the sum of x and y being 3; and phenmedipham, desmedipham, metamitron, lenacil, ethofumesate or chloridazon in association with a suitable carrier and/or surface active agent, and a method of combating weeds.

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Herbicidal compositions

This invention concerns new herbicidal compositions and methods of combating weeds.

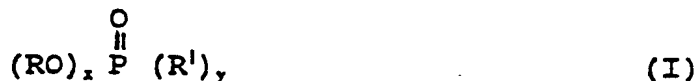
Prior Art

US Patent No 2927014 discloses phosphonates and phosphinates having herbicidal activity. We have now found that combinations of certain alkyl substituted phosphonates and phosphinates according to the US Patent with certain known sugar beet herbicides are surprisingly beneficial and synergistic.

Description

In one aspect, the invention provides a herbicidal composition comprising:

(a) at least one phosphonate or phosphinate of the formula:



where R and R¹, which may be the same or different, each represent straight or branch-chained alkyl of 1 to 12 carbon atoms, and x and y are each 1 or 2, the sum of x and y being 3; and

(b) at least one compound selected from phenmedipham, desmedipham, metamitron, lenacil, ethofumesate and chloridazon, or a combination of 2 and more; in association with a suitable carrier and/or surface active agent.

In another aspect, the invention provides a method of combating weeds which comprises applying to a locus

infested or liable to be infested therewith, an effective amount of the two components (a) and (b).

Preferred compounds of formula I are those wherein R and R¹ each represent 2-ethylhexyl or dodecyl, especially O,O-bis(2-ethylhexyl) (2-ethylhexyl) phosphonate.

The ratio by weight of (a) to (b) employed is preferably from 10:1 to 1:10, especially from 5:1 to 1:5.

The compositions of the invention are herbicidally-active against a wide range of broad-leaved and grass weeds, including Alopecurus, Echinochloa, Setaria, Amaranthus, Atriplex, Centaurea, Galium, Matricaria, Mercurialis, Polygonum and Stellaria species, but are comparatively safe to certain crop species, particularly beets. They may thus be of use as herbicides, and especially as selective herbicides, particularly in the control of a range of weeds in such crops.

The compositions of the invention usually contain from 0.01 to 99% by weight of the present compounds, and are normally produced initially as concentrates containing from 0.5 to 99%, preferably from 0.5 to 85%, and especially from 10 to 50% by weight thereof. Such concentrates are diluted if necessary before application to the locus to be treated such that the active ingredient comprises from 0.01 to 5% by weight of the formulation applied.

The carrier may be water, in which case an organic solvent may also be present, though this is not usually employed. A flowable suspension concentrate may be formed by grinding the compound with water, a wetting agent and a suspending agent, e.g. xanthan gum.

The carrier may alternatively be a water immiscible

organic solvent, e.g. a hydrocarbon which boils within the range 130-270°C, e.g. xylene, in which the compound is dissolved or suspended. An emulsifiable concentrate containing a water immiscible solvent may be formed with a surface active agent so that the concentrate acts as a self-emulsifiable oil on admixture with water.

The carrier may alternatively be a water-miscible organic solvent e.g. 2-methoxy ethanol, methanol, propylene glycol, diethylene glycol, diethylene glycol monoethyl ether, methylformamide or dimethylformamide.

The carrier may alternatively be a solid, which may be finely divided or granular. Examples of suitable solids are limestone, clays, sand, mica, chalk, attapulgite, diatomite, perlite, sepiolite, silicas, silicates, lignosulphonates and solid fertilizers. The carrier can be of natural or synthetic origin or can be modified natural material.

Wettable powders soluble or dispersible in water may be formed by admixing the compound in particulate form with a particulate carrier or spraying molten compound on to the particulate carrier, admixing a wetting agent and a dispersing agent and finely grinding the whole powder mixture.

An aerosol composition may be formed by admixing the compound with a propellant, e.g. a polyhalogenated alkane such as dichlorofluoromethane, and suitably also with a solvent.

The term 'surface active agent' is used in the broad sense to include materials variously called emulsifying agents, dispersing agents and wetting agents. Such agents are well known in the art.

The surface active agents used may comprise anionic surface active agents, for example mono- or di-esters of phosphoric acid with a fatty alcohol ethoxylate, or

salts of such esters, fatty alcohol sulphates such as sodium dodecyl sulphate, ethoxylated fatty alcohol sulphates, ethoxylated alkylphenol sulphates, lignin sulphates, petroleum sulphonates, alkylaryl sulphonates such as alkyl-benzene sulphonates or lower alkyl-naphthalene sulphonates, salts of sulphonated naphthaleneformaldehyde condensates, salts of sulphonated phenolformaldehyde condensates, or more complex sulphonates such as the amide sulphonates, e.g. the sulphonated condensation product of oleic acid and N-methyl taurine or the dialkyl sulphosuccinates e.g. the sodium sulphonate of dioctyl succinate.

The surface active agents may also comprise non-ionic agents, for example condensation products or fatty acid esters, fatty alcohols, fatty acid amides or alkyl-substituted phenols with ethylene oxide, fatty esters of polyhydric alcohol ethers e.g. sorbitan fatty acid esters, condensation products of such esters with ethylene oxide e.g. polyoxyethylene sorbitan fatty acid esters, block copolymers of ethylene oxide and propylene oxide, acetylenic glycols such as 2,4,7,9-tetramethyl-5-decyn-4,7-diol, or ethoxylated acetylenic glycols. The surface active agents may also comprise cationic agents, for example alkyl- and/or aryl-substituted quaternary ammonium compounds such as cetyl trimethylammonium bromide, or ethoxylated tertiary fatty amines.

Preferred surface active agents include ethoxylated fatty alcohol sulphates, lignin sulphonates, alkyl-aryl sulphonates, salts of sulphonated naphthaleneformaldehyde condensates, salts of sulphonated phenolformaldehyde condensates, sodium oleoyl N-methyltauride, dialkyl sulphosuccinates, alkyl phenol ethoxylates, and fatty alkyl ethoxylates.

If the components (a) and (b) are applied sequentially, they may each be applied in a composition analogous to those described above.

If desired, the compositions may contain one or more further active ingredients, eg herbicides, fungicides or insecticides in addition to components (a) and (b).

The present compound may be applied to plants, the soil, land or aquatic areas, and particularly to a locus at which a crop is growing. The method is particularly active post-emergence.

In the present method, the amount of (a) applied is preferably from 0.01 to 1 kg/ha, preferably from 0.05 to 0.25 kg/ha. The amount of (b) applied is preferably from 0.01 to 2 kg/ha, preferably from 0.05 to 0.5 kg/ha. The amount of (a) and (b) in total applied is preferably from 0.3 to 3 kg/ha.

Examples

The invention is illustrated by the following Examples in which the compounds employed are identified as follows:

- | | |
|-----|--|
| I | O,O-bis(2-ethylhexyl)
(2-ethylhexyl)phosphonate |
| II | phenmedipham |
| III | metamitron |
| IV | lenacil |
| V | chloridazon |
| VI | desmedipham |

and plant species are identified as follows:

- | | |
|---|--------------------------------|
| a | <u>Alopecurus myosuroides</u> |
| b | <u>Amaranthus retroflexus</u> |
| c | <u>Atriplex hortensis</u> |
| d | <u>Beta vulgaris altissima</u> |

e	<u>Beta vulgaris crassa</u>
f	<u>Beta vulgaris conditiva</u>
g	<u>Centaurea cyanus</u>
h	<u>Echinochloa crus-galli</u>
i	<u>Galium aparine</u>
j	<u>Matricaria chamomilla</u>
k	<u>Mercurialis annua</u>
l	<u>Setaria italica</u>
m	<u>Stellaria media.</u>

All rates of application are given as grams active ingredient per hectare (g a.i./ha).

Example 1

The compounds listed below were applied alone and in combination at the rates indicated to beets and weed seedlings grown in a greenhouse. Herbicidal effects were noted 6-10 days after application on a scale of from 0 (no effect) to 10 (complete kill).

Results obtained were as follows:

<u>Compds</u>	<u>Rate</u>	<u>a</u>	<u>i</u>	<u>j</u>	<u>k</u>	<u>d</u>	<u>f</u>
I	300	0.5	0.5	0.0	0.2	0.5	1.0
	1000	1.0	2.0	0.5	0.5	2.2	3.5
I+II	250 + 50	3.0	4.5	1.5	2.5	0.8	0.5
	200 + 100	4.5	7.0	4.0	1.5	0.8	0.5
	150 + 150	4.5	6.5	4.5	1.0	0.8	0.0
	100 + 200	4.0	6.5	4.5	2.0	1.0	0.0
	50 + 250	3.5	4.5	4.5	2.0	0.8	0.0
II	300	3.5	5.0	3.5	0.5	0.5	0.5
	1000	5.0	8.0	6.0	2.5	0.5	2.0

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<u>Compds</u>	<u>Rate</u>	<u>a</u>	<u>b</u>	<u>c</u>	<u>g</u>	<u>i</u>	<u>j</u>	<u>m</u>	<u>d</u>
I	300	0.5	3.0	1.0	1.0	0.5	0.0	1.0	0.5
	1000	1.0	3.5	2.5	1.5	2.0	0.5	1.5	2.2
I+III	250 + 50	1.0	3.0	3.0	2.0	2.0	3.5	2.0	1.2
	200 + 100	1.0	4.5	3.5	2.0	3.0	4.5	2.0	0.5
	150 + 150	2.0	4.5	4.5	1.5	4.0	5.0	2.0	0.8
	100 + 200	2.0	5.0	4.0	1.5	2.5	4.0	2.0	0.5
	50 + 250	1.5	4.0	3.0	1.0	2.0	3.0	2.5	0.4
III	300	0.5	2.5	0.5	1.5	0.5	3.0	0.0	0.2
	1000	4.0	3.5	2.5	2.5	1.5	6.0	0.5	0.2

Example 2

The compounds listed below were applied alone and in combination at the rates indicated to beets and weed seedlings grown in a greenhouse. The plants were harvested 8 to 14 days after treatment, and the harvested weights were measured. The percentage weight reductions relative to an untreated control were as follows:

<u>Compds</u>	<u>Rate</u>	<u>a</u>	<u>g</u>	<u>i</u>	<u>k</u>	<u>d</u>	<u>e</u>	<u>f</u>
I	300	5	0	32	8	5	2	0
	1000	12	4	42	0	12	5	0
I+II	250 + 50	37	19	80	7	2	3	2
	200 + 100	59	22	86	25	1	8	0
	150 +150	59	28	87	7	5	8	0
	100 +200	55	25	85	26	4	10	0
	50 + 250	57	22	85	48	0	6	1
II	300	52	23	79	16	0	3	0
	1000	67	39	92	29	4	24	16

SUBSTITUTE SHEET

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<u>Compds</u>	<u>Rate</u>	<u>b</u>	<u>c</u>	<u>g</u>	<u>i</u>	<u>m</u>	<u>d</u>	<u>e</u>	<u>f</u>
I	300	12	2	0	32	4	5	2	0
	1000	23	39	4	42	14	12	5	0
I+III	250 + 50	27	53	10	55	36	4	4	0
	200 + 100	41	62	15	69	50	0	7	0
	150 + 150	46	73	19	70	54	0	0	6
	100 + 200	50	69	19	69	54	0	2	0
	50 + 250	47	53	17	61	46	0	1	0
III	300	18	6	7	45	24	0	3	0
	1000	51	55	23	70	53	0	0	0
Control		0	0	0	0	0	0	0	0

<u>Compds</u>	<u>Rate</u>	<u>c</u>	<u>h</u>	<u>i</u>	<u>l</u>	<u>m</u>	<u>d</u>	<u>f</u>
I	300	2	0	32	23	4	5	0
	1000	39	20	42	46	14	12	0
I+IV	250 + 50	4	21	36	27	1	0	0
	200 + 100	12	25	45	41	14	3	0
	150 + 150	37	28	54	41	16	12	4
	100 + 200	57	27	58	46	17	13	4
	50 + 250	40	26	50	41	26	4	5
IV	300	0	16	17	25	3	0	0
	1000	15	32	34	33	13	0	0
Control		0	0	0	0	0	0	0

SUBSTITUTE SHEET

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<u>Compds</u>	<u>Rate</u>	<u>b</u>	<u>c</u>	<u>g</u>	<u>h</u>	<u>i</u>	<u>l</u>	<u>m</u>	<u>f</u>
I	600	15	20	4	12	15	26	8	0
	2000	30	70	25	57	14	32	33	5
I+V	500 + 100	57	81	17	48	69	54	40	6
	400 + 200	74	83	16	49	74	55	43	11
	300 + 300	65	82	17	57	76	56	50	7
	200 + 400	68	83	18	52	74	47	41	9
	100 + 500	46	77	17	50	64	41	35	2
V	600	18	22	3	35	30	23	15	0
	2000	42	49	22	59	45	41	39	2
Control		0	0	0	0	0	0	0	0

<u>Compds</u>	<u>Rate</u>	<u>a</u>	<u>c</u>	<u>g</u>	<u>i</u>	<u>j</u>	<u>m</u>	<u>f</u>
I	500	10	0	0	0	13	6	7
	1000	31	50	8	0	20	56	27
I+VI	300 + 200	50	73	46	62	59	78	0
	600 + 400	66	86	67	81	76	89	30
VI	500	28	36	45	51	60	65	2
	1000	55	73	58	75	68	84	32
Control		0	0	0	0	0	0	0

SUBSTITUTE SHEET

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<u>Compds</u>	<u>Rate</u>	<u>a</u>	<u>c</u>	<u>g</u>	<u>i</u>	<u>h</u>	<u>i</u>	<u>e</u>
I	680	14	31	0	13	19	0	27
I+II	680 + 450	55	71	57	79	71	90	13
II	450	18	1	16	48	18	40	0
Control		0	0	0	0	0	0	0

<u>Compds</u>	<u>Rate</u>	<u>a</u>	<u>h</u>	<u>i</u>	<u>i</u>	<u>m</u>	<u>d</u>
I	300	0	0	0	0	4	5
	1000	19	27	17	6	8	10
I+II+VI	193 + 53.5 + 53.5	35	85	79	50	33	0
	430 + 120 + 120	46	86	90	70	43	9
II+VI	150 + 150	18	72	54	32	18	0
	335 + 335	41	79	80	53	28	2
Control		0	0	0	0	0	0

Example 3:

The compounds listed below were applied alone and combination at the rates indicated to beets and weed seedlings grown in a greenhouse. Herbicidal effects were noted 6 - 10 days after application on a scale from 0 (no effect) to 10 (complete kill). Results were obtained as follows:

a) <u>with compound VII</u>	<u>g a.i./ha</u>	<u>m</u>
ethofumesate VII	600	4.0

VII	500	
+	+	5.0
diethylmethylphosphonate	100	
(ZK 146 953) (VIII)		
VII + VIII	400	
	+	4.5
	00	
VIII	600	0.1
VII	500	
+	+	4.5
diethylethylphosphonate	100	
(ZK 53 491) (IX)		
VII + IX	400	
	+	4.5
	200	
IX	600	0.2

b)	with compound II	g a.i./ha	j
	II	300	3.5
<hr/>			
	II +	100 + 200	6.5
	dipentylpentylphosphonate	150 + 150	4.0
	(ZK 148 236) (X)		
	X	300	0
	II +	200 + 100	5
	dibutylbutylphosphonate	100 + 200	5.5
	(ZK 147 326) (XI)		
	(XI)	300	0.5
	II +	200 + 100	5
	diisopropylallylphosphonate	100 + 200	5.5
	(ZK 147 327) (XII)		
	XII	300	0
	II +	200 + 100	4.0
	diisopropylmethylphosphonate	100 + 200	4.5
	(ZK 146 952) (XIII)		
	XIII	300	0

CLAIMS

1. A herbicidal composition comprising:
(a) at least one phosphonate or phosphinate of the formula:



where R and R', which may be the same or different, each represent straight or branch-chained alkyl of 1 to 12 carbon atoms, and x and y are each 1 or 2, the sum of x and y being 3; and

- (b) at least one compound selected from phenmedipham, desmedipham, metamitron, lenacil, ethofumesate and chloridazon, or a combination of 2 and more; in association with a suitable carrier and/or surface active agent.
2. A composition according to claim 1 in which each R and R' group in the compound of formula I is 2-ethylhexyl or dodecyl.
3. A composition according to claim 1 or claim 2 in which x in the compound of formula I is 2.
4. A composition according to any of claims 1 to 3 in which the ratio by weight of component (a) to component (b) is from 1:10 to 10:1.
5. A composition according to claim 4 in which the ratio by weight of component (a) to component (b) is from 1:5 to 5:1.
6. A method of combating weeds which comprises applying to a locus infested or liable to be infested therewith, an effective amount of the two components (a) and (b) as defined in claim 1.
7. A method according to claim 6 in which the components (a) and (b) are applied in the form

of a composition according to any of claims 1 to 5.

8. A method according to claim 6 or claim 7, in which the amount of component (a) applied is from 0.01 to 1 kg/ha.
9. A method according to any of claims 6 to 8 in which the amount of (b) applied is from 0.01 to 2 kg/ha.
10. A method according to any of claims 6 to 9 in which the total amount of components (a) and (b) applied is from 0.3 to 3 kg/ha.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 92/01973

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 A01N57/20; //(A01N57/20,47:22, 43:707,43:54, 43:12, 43:58)		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	A01N	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US,A,2 927 014 (L.E.GOYETTE) 1 March 1960 cited in the application -----	
<p>¹⁰ Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
13 NOVEMBER 1992	14. 12. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	DONOVAN T.M.	

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EP 9201973
SA 63904

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-2927014		None	

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